1952 *Inorg. Chem.* **1990**, *29*, 1952–1957

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Electrochemistry and Redox Chemistry of $H_2OFe^{III}SiW_{11}O_{39}{}^{5-}$ in the Presence of H_2O_2 and OH

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Received August 3, 1989

Heteropolytungstates in which one of the positions normally occupied by a tungsten cation is occupied instead by an iron cation are shown to be catalysts for the electroreduction of H_2O_2. The rate constant governing the reduction of H_2O_2 by $H_2OFe^{II}SiW_{11}O_{39}{}^{6-}$ was measured by stopped flow as $9 \times 10^2\ M^{-1}\ s^{-1}$. A catalytic mechanism involving an Fe(IV) intermediate generated from the reaction between the Fe(III) form of the heteropolytungstate anion and hydroxyl radicals is presented. The Fe(IV) intermediate can react with itself to produce H_2O_2 and the Fe(III) form of the heteropolytungstate. Alternatively, the Fe(IV) intermediate can consume additional H_2O_2 by oxidizing it to O_2. Competition between these two reaction pathways accounts for the nonintegral stoichiometry observed under some experimental conditions during the electroreduction of H_2O_2 catalyzed by $H_2OFe^{II}SiW_{11}O_{39}{}^{6-}$. Pulse-radiolysis experiments were employed to detect the Fe(IV) intermediate, to evaluate rate constants for the reactions in which it is formed and decomposed, and to measure the rate of reduction of the Fe(III) form of the heteropolytungstate by $O_2{}^-$.

With the goal of identifying electrocatalytically active transition-metal complexes that are more resistive to oxidizing environments than are those based on organic ligands, we have been examining the electrochemistry of transition-metal-substituted heteropolytungstates.[1,2] The initial studies involved a series of iron-substituted anions, $H_2OFe^{III}XW_{11}O_{39}{}^{n-}$, where X represents a tetrahedrally coordinated heteroatom (Si, Ge, P, As) surrounded by four triads of tungsten–oxo octahedra.[3] The resulting polynuclear structure retains its integrity in aqueous media over a broad pH range ($2 < pH < 8$), and the entirely inorganic complexes are inert toward oxidizing agents that often degrade complexes containing organic ligands. In the $H_2OFe^{III}XW_{11}O_{39}{}^{n-}$ complexes, the tungsten–oxo framework provides a vacant coordination site composed of five oxo groups in which the Fe(III) center sits. The sixth coordination position of the Fe(III) cation is occupied by a substitutionally labile water molecule (which is converted to a hydroxide ion at higher pH values, e.g., pH 6 for X = Si[1,3]). Suitable substrates may displace the labile water molecule on the iron center so that electron transfer between the heteropolyanion and reducible or oxidizable substrates may proceed by inner-sphere mechanisms that are not available to the more commonly studied, unsubstituted anions such as $SiW_{12}O_{40}{}^{4-}$.[4]

The catalytic utility and robustness of the $H_2OFe^{III}SiW_{11}O_{39}{}^{5-}$ anion were demonstrated in a previous study of the electrocatalytic reduction of nitrite and nitric oxide.[2] The anion is also catalytically active toward the electroreduction of H_2O_2, where highly oxidizing hydroxyl radicals are likely intermediates. We undertook a study of this system to expand the range of substrates for which kinetic data on the catalytic efficiency of this class of catalyst are available as well as to assess their resistance to oxidative degradation by hydroxyl radicals. The electrochemical experiments revealed reactions of the catalyst that differed substantially from those proposed for other catalysts for the electroreduction of H_2O_2 such as $Fe(OH_2)_6{}^{3+}$.[5] A short-lived form of the catalyst with the iron center oxidized to an oxidation state above +3 was implicated. Pulse-radiolysis experiments were successful in detecting the indicated intermediate and allowed its rate of formation and disappearance as well as some of its redox reactions to be monitored. This report summarizes the result of the electrochemical and pulse-radiolysis experiments and utilizes the results of the latter to rationalize the unusual behavior observed in the former set of experiments.

Experimental Section

Materials. The heteropolytungstate anions were prepared and purified as previously described.[1,3] Other chemicals for electrochemical experiments were reagent grade and used as received. Stock solutions of H_2O_2 were analyzed regularly by titration with standard solutions of $KMnO_4$.[6] All solutions were prepared with water which, after distillation, was passed through a Milli-Q purification system.

The pulse-radiolysis experiments were carried out with solutions containing 0.1 M sodium perchlorate and 2–50 mM phosphate. Their pH was adjusted by addition of small amounts of $HClO_4$ or NaOH. The chemicals and gases ($NaClO_4 \cdot H_2O$, G. F. Smith Chemical Co.; HCOONa, "Baker Analyzed" reagent; NaOH, G. F. Smith Co. Ultrapure 99.999%; $HClO_4$, Vycor Distilled, G. F. Smith Chemical Co.; KH_2PO_4, J. T. Baker Chemical Co., Ultrex; N_2O and O_2, both UHP grade from MG Gases Ltd.) were used as received.

Apparatus and Procedures. The electrochemical instrumentation and procedures employed have been described.[1] Polished, glassy-carbon electrodes (Tokai Co., Tokyo) were utilized for cyclic voltammetry and rotating-disk voltammetry. Controlled-potential electrolytes were conducted at a stirred mercury pool electrode. Potentials were measured and are reported with respect to a sodium chloride saturated calomel electrode (SSCE) except where noted. Experiments were conducted at ambient laboratory temperatures (20–23 °C).

Upon radiolysis of water with ionizing radiation (^{60}Co γ rays or 2-MeV electrons) the following radicals and molecular products are formed:

$$H_2O \rightsquigarrow HO\ (2.75),\ e_{aq}{}^-\ (2.65),\ H\ (0.65),\ H_2O_2\ (0.72),\ H_2\ (0.45) \qquad (1)$$

where the values in parentheses are *G* values, that is, the number of

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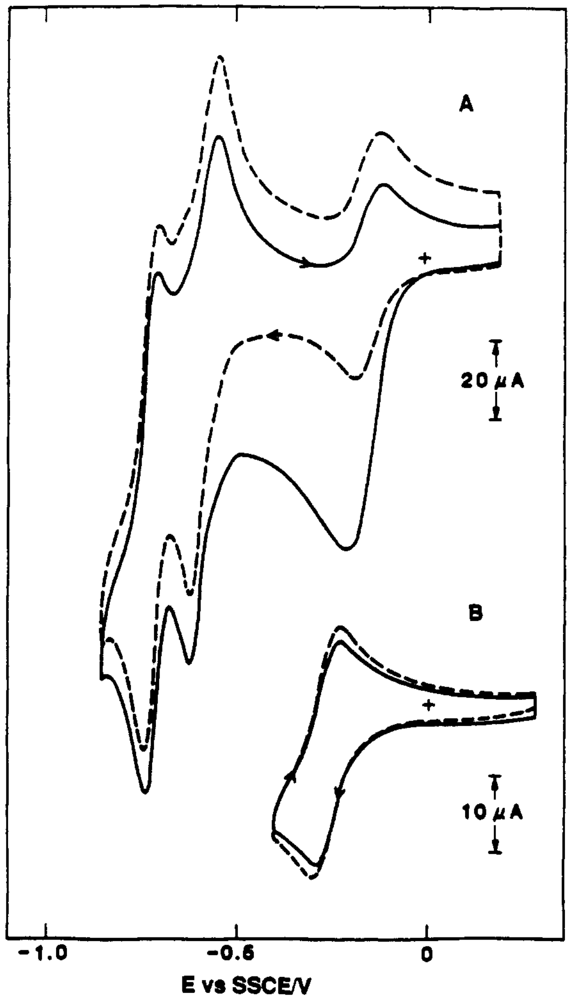

Figure 1. Cyclic voltammograms of 1 mM solutions of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ (A) and $SiW_{12}O_{40}^{4-}$ (B) in the absence (---) and in the presence (—) of 1 mM H_2O_2. Scan rate = 50 mV s^{-1}. Supporting electrolyte: 0.1 M $NaClO_4$ + 0.01 M $HClO_4$.

species formed when 100 eV of energy is dissipated in water.[7] Saturation of an aqueous solution with N_2O at pH > 4 results in the effective conversion of all e_{aq}^- to OH radicals by the well-established mechanism $e_{aq}^- + N_2O + H_2O \rightarrow N_2 + OH + OH^-$, for which the rate constant is 8.7×10^9 M^{-1} s^{-1}.[8] Added formate reacts rapidly with both OH and H yielding the CO_2^- radical ($OH + HCOO^- \rightarrow H_2O + CO_2^-$; $k = 3.2 \times 10^9$ M^{-1} s^{-1}).[9] The hydrated electron reacts with the proton at a diffusion-controlled rate yielding H atoms ($e_{aq}^- + H^+ \rightarrow H$; $k = 10^{10}$ M^{-1} s^{-1}). The O_2^-/O_2H radicals (pK = 4.8) are formed either by direct oxygen scavenging of the primary reducing radicals ($e_{aq}^-/H + O_2 \rightarrow O_2^-/O_2H$; $k = 2.0 \times 10^{10}$ M^{-1} s^{-1}) or via the reaction of the CO_2^- radical with O_2 ($CO_2^- + O_2 \rightarrow CO_2 + O_2^-$; $k = 5.0 \times 10^9$ M^{-1} s^{-1}).[10]

Pulse-radiolysis experiments were carried out with the BNL 2-MeV Van de Graaff accelerator according to procedures described elsewhere.[11] Calibration of the energy deposition was done with the KSCN dosimeter taking $G((SCN)_2^-) = 6.13$ and $\epsilon_{472} = 7950$ M^{-1} cm^{-1}.[12]

Steady-state radiolyses were performed in a ^{60}Co γ-ray source that had been calibrated with the ferrous dosimeter by using $G(Fe^{3+}) = 15.5$,[13] the energy flux at the time of the experiments was 1.0 krad/min or 1.0×10^{-7} M of OH radicals/s. All peroxide concentrations of radiolyzed solutions were determined with the KI method.[14]

Stopped-flow experiments were performed under nitrogen with a Durrum Instruments Model No. D-110 stopped-flow spectrophotometer that was interfaced to an OLIS computerized data evaluation system.

Results

Electrochemistry of $H_2OFeSiW_{11}O_{39}^{5-}$ in the Presence of H_2O_2. The electrochemical responses exhibited by the $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ anion in the absence of reducible substrates have been described in a previous study.[1] The dashed curve in Figure 1A is a representative cyclic voltammogram which consists of three reversible couples. The response at the most positive potential involves the one-electron Fe^{III}/Fe^{II} couple, and the two waves at more negative potentials arise from separated, two-electron reductions of the tungsten–oxo framework. Addition of H_2O_2 to the solution of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ produced a large increase in the cathodic peak current at the potential where the Fe(III) center is reduced to Fe(II) (Figure 1A, solid line) and the catalyzed reduction of H_2O_2 ensued. It is clear that the Fe center plays an essential role in the catalytic mechanism because the cyclic voltammetry of the unsubstituted $SiW_{12}O_{40}^{4-}$ anion, which has a one-electron reduction wave at almost the same potential as that for the $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ derivative, showed no evidence of a catalytic reduction when H_2O_2 was added (Figure 1B). (The reduced, iron-free anion, $SiW_{12}O_{40}^{5-}$, does react slowly with H_2O_2, but the reaction rate is too low to affect cyclic voltammetric responses at scan rates of 100 mV s^{-1}.)

Mixtures of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ and H_2O_2 are stable over long periods. Controlled-potential electrolyses of such mixtures at -0.4 V, where the Fe(III) center in the catalyst is reduced to Fe(II), proceeded smoothly, but the number of electrons consumed per H_2O_2 molecule varied between ca. 0.9 and 2 and depended on a variety of experimental parameters including the relative concentrations of the catalyst and H_2O_2, the pH, the rate of stirring of the solution, and the rate with which argon was bubbled through the solution. The catalyst was unaffected by extensive cycling during electrolytic reductions, as judged by its cyclic voltammetry before and after the electrolysis. The variable quantity of charge consumed during the electrolysis contrasts with the behavior observed when $Fe(OH_2)_6^{3+}$ is employed as catalyst for the electroreduction of H_2O_2:[5] Two electrons are consumed by each H_2O_2 molecule according to a proposed reaction sequence in which hydroxyl radicals produced in the first step are quantatively reduced by Fe(II) in a rapid second step.[5] When the electroreduction was carried out with the $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ catalyst at more negative potentials, where the two-electron reduction of the tungsten–oxo framework proceeds along with the reduction of the Fe(III) center to produce a species capable of transferring more than one electron, two electrons per H_2O_2 molecule were required. The consumption of fewer than two electrons per H_2O_2 molecule during the catalyzed electroreduction of H_2O_2 at potentials where only the Fe(III) center of the $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ anion is reduced suggests the existence of a reaction pathway involving the iron center in which the hydroxyl radicals generated in the primary reaction between H_2O_2 and $H_2OFe^{II}SiW_{11}O_{39}^{6-}$ are diverted into a reaction other than further reduction by a second $H_2OFe^{II}SiW_{11}O_{39}^{6-}$ anion. This alternative reaction pathway will be examined in more detail in the Discussion section.

In a separate set of experiments, the rate of reaction between H_2O_2 and $H_2OFe^{II}SiW_{11}O_{39}^{6-}$ was measured by using stopped-flow techniques. The reaction was examined with large excesses of the reduced anion present, which avoided the complications of nonintegral stoichiometry encountered in the electrochemical measurements. Clean second-order kinetics were observed ($k = (9 \pm 0.3) \times 10^2$ M^{-1} s^{-1}) which were consistent with a slow initial step producing a hydroxyl radical that was subsequently rapidly reduced by a second $H_2OFe^{II}SiW_{11}O_{39}^{6-}$ anion.

It also proved instructive to carry out electroreductions of H_2O_2 as catalyzed by $Fe(OH_2)_6^{3+}$ in the presence of the $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ or $SiW_{11}O_{40}^{4-}$ anions. In the absence of the heteropolytungstates the electroreductions of the H_2O_2 followed a simple two-electron pathway as described in previous reports.[5] In the absence of H_2O_2, addition of either heteropolytungstate was without effect on the voltammetric response of the Fe-

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Table I. Inhibition by $H_2OFe^{III}SiW_{11}O_{39}{}^{5-}$ of the Electroreduction of H_2O_2 As Catalyzed by $Fe(OH_2)_6{}^{2+}$

exp no.	soln compn[a]	I_D, μA[b]
1	6 mM $Fe(OH_2)_6{}^{2+}$	191[c]
2	exp 1 + 6 mM H_2O_2	260
3	exp 2 + 3 mM $Fe^{III}SiW_{11}O_{39}{}^{5-}$	225
4	exp 2 + 3 mM $SiW_{12}O_{40}{}^{4-}$	262

[a] Supporting electrolyte: 0.1 M $NaClO_4$ + 0.01 M $HClO_4$. [b] Plateau current at a glassy-carbon disk electrode rotated at 100 rpm. The current was measured at ca. 0.3 V. [c] Essentially the same plateau current was obtained in the presence of 3 mM $H_2OFe^{III}SiW_{11}O_{39}{}^{5-}$ or 3 mM $SiW_{12}O_{40}{}^{5-}$.

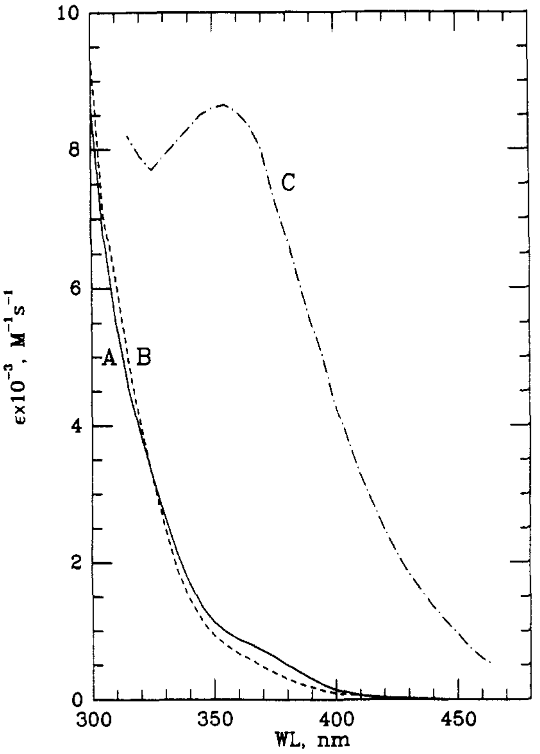

Figure 2. Absorption spectra: (A) 0.1 mM $H_2OFe^{III}SiW_{11}O_{39}{}^{5-}$ (pH 4.0); (B) 0.1 mM $H_2OFe^{III}SiW_{11}O_{39}{}^{6-}$ (pH 6.6); (C) transient complex formed during pulse radiolysis of the solution in (B). Supporting electrolyte: 100 mM $NaClO_4$ + 26 mM N_2O + 2 mM phosphate. Average concentration of hydroxyl radicals generated: 3.3 μm. T = 24 °C.

$(OH_2)_6{}^{3+/2+}$ couple, which occurs at a much more positive potential ($E_{1/2}$ = 0.50 V) than the first reduction wave of $H_2OFeSiW_{11}O_{39}{}^{5-}$ ($E_{1/2}$ = −0.15 V) or of $SiW_{12}O_{40}{}^{4-}$ ($E_{1/2}$ = −0.27 V). However, the $H_2OFe^{III}SiW_{11}O_{39}{}^{5-}$ anion, but not the $SiW_{12}O_{40}{}^{4-}$ anion, produced a significant decrease in the catalytic current for the reduction of H_2O_2 (Table I). The behavior is consistent with the interception of the hydroxyl radicals generated in the reaction between $Fe(OH_2)_6{}^{2+}$ and H_2O_2 by the $Fe^{III}SiW_{11}O_{39}{}^{5-}$ anion to produce an oxidized intermediate that may either consume H_2O_2 by oxidation or be reduced by a second $Fe(OH_2)_6{}^{2+}$ ion.

The proposed oxidation by hydroxyl radicals of the Fe(III) centers in $H_2OFe^{III}SiW_{11}O_{39}{}^{5-}$ is similar to behavior described in a recent pulse-radiolytic study of the reaction between OH and $Fe(OH)_4{}^-$.[15] We therefore carried out analogous experiments in which OH radicals were generated in solutions containing the $H_2OFe^{III}SiW_{11}O_{39}{}^{5-}$ anions.

Pulse Radiolysis of $H_2OFe^{III}SiW_{11}O_{39}{}^{5-}$. Solutions of $H_2OFe^{III}SiW_{11}O_{39}{}^{5-}$ (0.031–2 mM) at pH ≥4 were saturated with N_2O and pulse irradiated with 2-Mev electrons. Under these conditions all $e_{aq}{}^-$ are converted into OH radicals (vide supra), which react with $H_2OFe^{III}SiW_{11}O_{39}{}^{5-}$ to produce a short-lived species that has an absorption band between 320 and 430 nm (λ_{max} = 355 nm; ϵ_{355} = 8,600 ± 800 $M^{-1}\ cm^{-1}$) (Figure 2C). The growth of the absorption was monitored at different wave lengths (320–430 nm) and used to evaluate the rate constants for the formation and decomposition reactions (Table II). The rate of formation of the intermediate was measured under pseudo-first-order conditions (excess $H_2OFe^{III}SiW_{11}O_{39}{}^{5-}$) and found to be first order with respect to both OH radicals and the iron-substituted heteropolytungstate anion and independent of wavelength.

Table II. Rate Constants for the Formation and Subsequent Decomposition of the Intermediate Formed in the Reaction between Hydroxyl Radicals and $H_2OFe^{III}SiW^{11}O_{39}{}^{5-}$[a]

$[H_2OFe^{III}SiW_{11}O_{39}{}^{5-}]$, mM	pH	$10^{-8}k_f$,[b,d] $M^{-1}\ s^{-1}$	$10^{-9}k_d$,[c,d] $M^{-1}\ s^{-1}$
2.0	4	5.3	3.0
1.0	4	4.0	3.2
0.5	4	6.4	3.1
0.25	4	5.2	3.3
0.125	4	5.0	3.5
0.062	4	5.8	4.5
0.031	4	5.3	5.8
		5.2 ± 0.5[e] (av)	3.2 ± 0.1[e] (av)
2.0	7	4.7	2.4
1.0	7	5.0	2.2
0.5	7	4.6	2.0
0.25	7	6.3	2.2
0.125	7	7.0	3.5
0.062	7	5.2	4.0
		5.5 ± 0.9[e] (av)	2.5 ± 0.4[e] (av)
0.5	6.2	5.6	
0.5	5.9	5.6	
0.5	5.5	5.5	
0.5	5.0	5.7	
0.5	4.8	5.7	
0.5	4.3	6.2	

[a] Reaction conditons: Supporting electrolyte 100 mM $NaClO_4$ + 2 mM phosphate. The anion is converted to $HOFe^{III}SiW_{11}O_{39}{}^{6-}$ at pH ≥7. Concentrations of OH radicals varied between 1 and 10 μM. [b] Second-order rate constants for the formation of the intermediate. [c] Second-order rate constant for the decomposition of the intermediate. [d] Rate constants were typically reproducible to ±10–15%. However, we occasionally observed larger deviations with different samples of the heteropolytungstates for reasons we were unable to establish. The values in the table are representative. [e] Average values were calculated by omitting concentrations below 0.125 mM.

At the highest concentrations of $H_2OFe^{III}SiW_{11}O_{39}{}^{5-}$ employed (2 mM), the formation of the intermediate was both faster than the competing dimerization of OH ($k = 5 \times 10^9$ $M^{-1}\ s^{-1}$, but [OH] ~ 10^{-6} M[16]) and complete before its bimolecular decomposition became significant. The absorbance observed under these conditions was used to estimate the molar absorption coefficients between 400 and 450 nm. Since the spectral data between 325 and 400 nm were obtained under conditions where the competing reactions mentioned above were significant, the observed absorbances were normalized by utilizing calibration curves (absorbance vs energy input at varying concentrations of the complex). The spectrum has also been corrected for the absorbance of the parent, unreacted $H_2OFe^{III}SiW_{11}O_{39}{}^{5-}$ anion, which is given for reference at both pH 4 (Figure 2A) and pH 6.6 (Figure 2B). The spectrum of the intermediate showed no change with pH in the region between pH 4 and 7. Experiments with the isomorphous $H_2OFe^{III}AsW_{11}O_{39}{}^{4-}$ anion produced kinetic data similar to those in Table II and a spectrum that closely resembled the one in Figure 2. Since no spectral changes were observed when similar concentrations of the unsubstituted $SiW_{12}O_{40}{}^{4-}$ anion were exposed to OH radicals, the Fe(III) center appears to be the site of OH radical attack on the iron-substituted heteropolytungstate complexes. Hence, for purposes of exposition, we will regard the transient intermediate derived from the iron-substituted complexes as a complex of Fe(IV) without intending to rule out alternative

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Table III. Rate Constants for the Reaction of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ with O_2^{-} [a]

$[H_2OFe^{III}SiW_{11}O_{39}^{5-}]$,[b] mM	pH	$10^{-8}k$,[c] $M^{-1}\ s^{-1}$
20	7	3.3
10	7	4.5
5	7	3.2
		3.7 ± 0.7 (av)
20	8	1.7
10	8	1.8
5	8	1.3
		1.6 ± 0.3 (av)

[a] Supporting electrolyte: 100 mM HCOONa + 50 mM phosphate + 1.2 mM O_2. [b] The anion is converted to $HOFe^{III}SiW_{11}O_{39}^{6-}$ at pH 7 and 8. [c] Rate constants were typically reproducible to ±20%.

possibilities such as an OH adduct of the Fe(III) complex.

The rate of decomposition of the Fe(IV) intermediate is second order in Fe(IV) and independent of the concentration of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ in the range between 0.125 and 2 mM. At lower concentrations the decomposition rate constant shows some dependence on the concentration of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ (Table II).

In the absence of the heteropolyanions, the yields of H_2O_2 measured in irradiated solutions saturated with N_2O were in agreement with the expected yields of $G(H_2O_2) = G_{H_2O_2} + 0.5G_{OH}$.[7] In the presence of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ at pH 2.4 the concentration of H_2O_2 generated during the pulse ratiolysis of a N_2O saturated solution was identical with that produced in the absence of the complex. This observation indicates strongly that the decomposition of the Fe(IV) complex produces H_2O_2 just as does the dimerization of the OH radicals generated in the absence of the heteropolytungstate anion.

The reduction of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ by O_2^{-} was studied at pH 7 and 8 by monitoring the growth of $H_2OFe^{II}SiW_{11}O_{39}^{6-}$ at 450 nm ($\epsilon_{450} = 200\ M^{-1}\ cm^{-1}$; see Table III for conditions and rate data). The O_2^{-}/O_2H radicals were generated with $G = 6.1$ in oxygen-saturated (1.2 mM) formate solutions, as described in the Experimental Section. The rate of formation of the $H_2OFe^{II}SiW_{11}O_{39}^{6-}$ complex was first order in both O_2^{-} and $H_2OFe^{III}SiW_{11}O_{39}^{5-}$. Average rate constants of $(1.6 \pm 0.3) \times 10^3\ M^{-1}\ s^{-1}$ and $(3.7 \pm 0.7) \times 10^3\ M^{-1}\ s^{-1}$ were measured at pH 8 and 7, respectively. The pH dependence of the rate constants is in the direction expected from the pH dependence of the formal potentials of the Fe(III/II) couple for the anion[1] and therefore on the driving force of the reaction.

Attempts to examine the kinetics of the reduction of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ by O_2^{-}/O_2H at pH 2 were unsuccessful. The reaction does proceed and $H_2OFe^{II}SiW_{11}O_{39}^{6-}$ is formed, but very complex reaction kinetics were encountered that could not be satisfactorily resolved.

Steady-State Radiolysis of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$. A ^{60}Co source was utilized to provide continuous radiolysis of solutions saturated with N_2O and also containing 0.5 mM $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ and ca. 0.4 mM H_2O_2. Hydroxyl radicals were generated in the solution at the steady rate of 10^{-7} M s^{-1} ($G = 6.0$), from which a steady-state concentration of the Fe(IV) complex of ca. 6×10^{-9} M can be calculated by using the decomposition rate constant in Table II. With these concentrations, almost all of the OH radicals generated during the radiolysis react with the $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ ($k_f = 7 \times 10^8\ M^{-1}\ s^{-1}$) to produce the Fe(IV) anion instead of with H_2O_2 ($k = 4.5 \times 10^7\ M^{-1}\ s^{-1}$ [17]). This system was utilized to examine the reaction of the Fe(IV) complex with H_2O_2. The changes in the concentration of H_2O_2 during steady-state radiolysis experiments at pH 2 and at pH 7 are shown in Figure 3. Solutions containing H_2O_2 and $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ are stable under these conditions, and no change in the concentrations of H_2O_2 was observed in the absence of radiolysis. Throughout the radiolysis, H_2O_2 is formed at a low rate by direct recombination of OH radicals in the spur for which $G = 0.7$.[7] Thus, even if the Fe(IV) complex formed in the reaction between the radiolytically generated OH radicals and the $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ anions were stable, an increase in the H_2O_2 concentration would be expected to occur during the radiolysis.[7] The expected increase for this case is shown as the dashed line in Figure 3. Experimentally, a decrease in the concentration of H_2O_2 was observed, which indicates that the reaction in which the Fe(IV) complex oxidizes H_2O_2 proceeds more rapidly than the second-order decomposition of the Fe(IV) anion to produce $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ and H_2O_2.

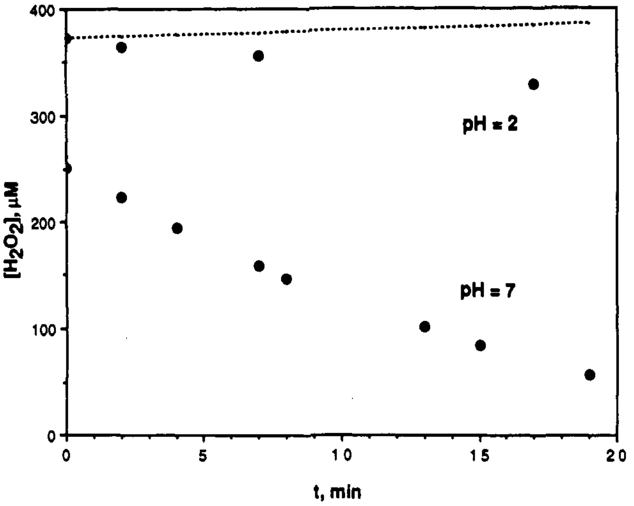

Figure 3. Variation in the concentration of H_2O_2 in a 0.5 mM solution of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ during its steady-state radiolysis with a ^{60}Co source. Supporting electrolyte: 0.1 M $NaClO_4$. The rate at which H_2O_2 is generated by direct recombination of OH radicals in the spur is indicated by the dashed line.

The upper set of points plotted in Figure 3 are the measured concentrations of H_2O_2 during steady-state radiolysis at pH 2. Because of the complications associated with the generation of H atoms as well as OH radicals at this low pH, we did not attempt to analyze these data. When the experiment was repeated at pH 5–7, the rate of decrease in the concentration of H_2O_2 was considerably greater, as shown by the lower set of experimental points plotted in Figure 3. In fact, the rate of decrease of the H_2O_2 concentration exceeded the rate at which the Fe(IV) anion was produced in the radiolysis so that a chain reaction leading to the decomposition of H_2O_2 was indicated by the more rapid disappearance of H_2O_2 at these higher pH values.

Discussion

Basis of the Electrocatalytic Behavior of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ Anions. The measured rate constant for the reaction between $H_2OFe^{II}SiW_{11}O_{39}^{6-}$ and H_2O_2 of $9 \times 10^2\ M^{-1}\ s^{-1}$ is only 1 order of magnitude greater than the reported value for the reaction of H_2O_2 with $Fe(OH_2)_6^{2+}$ [18] despite the large difference (680 mV) in the reducing power of the two reductants. This insensitivity to driving force argues against an outer-sphere mechanism for the reaction.

The catalysis of the electroreduction of H_2O_2 by iron-substituted heteropolytungstates exhibits the hallmarks of an inner-sphere mechanism that requires participation by the iron center. On the cyclic voltammetric time scale, no catalysis is observed with the iron-free parent anion $SiW_{12}O_{40}^{4-}$, even though this species undergoes a one-electron reduction at a potential very close to that of the one-electron reduction of the catalytically active $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ anion (Figure 1). The reduced form of the former anion, $SiW_{12}O_{40}^{5-}$, possesses an electron energetic enough to reduce H_2O_2 but lacks a site for the H_2O_2 to coordinate to the catalyst. The significant catalytic current obtained with the iron-substituted anion (at the same potential where there is no evidence of catalysis in the voltammogram for the $SiW_{12}O_{40}^{4-}$ anion) therefore seems clearly to depend upon an inner-sphere

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(17) Schwarz, H. A. *J. Phys. Chem.* **1962**, *66*, 255.

(18) Conocchioli, T. J.; Hamilton, E. J.; Sutin, N. *J. Am. Chem. Soc.* **1965**, *87*, 926. Wells, C. F.; Salam, M. A. *Trans. Faraday Soc.* **1967**, *63*, 620.

pathway in which the substrate replaces the single, substitutionally labile water molecule in the coordination sphere of the iron center. Additional evidence favoring this description is the decrease in the magnitude of catalytic currents for the reduction of H_2O_2 in the presence of ligands such as pyridine, which can compete with H_2O_2 for the coordination site on the iron center but produce insignificant changes in the formal potential of the catalyst. Thus, a plausible catalytic mechanism in the presence of excess catalyst is the following:

$$H_2OFe^{III}SiW_{11}O_{39}^{5-} + e^- \rightleftarrows H_2OFe^{II}SiW_{11}O_{39}^{6-} \quad (2)$$

$$H_2OFe^{II}SiW_{11}O_{39}^{6-} + H_2O_2 \rightleftarrows H_2O_2Fe^{II}SiW_{11}O_{39}^{6-} + H_2O \quad (3)$$

$$H_2O_2Fe^{II}SiW_{11}O_{39}^{6-} \rightarrow HOFe^{III}SiW_{11}O_{39}^{6-} + OH \quad (4)$$

$$OH + H_2OFe^{II}SiW_{11}O_{39}^{6-} + H^+ \xrightarrow{\text{fast}} H_2O + H_2OFe^{III}SiW_{11}O_{39}^{5-} \quad (5)$$

The order of the initial electron transfer and coordinative displacement steps could be inverted, and the final, fast reaction is written as an outer-sphere electron-transfer process but could also be written as a hydrogen atom transfer reaction followed by intramolecular electron transfer and protonation.

The mechanism embodied in reactions 2–5 requires that two electrons be consumed by each H_2O_2 molecule, as is observed in the presence of excess catalyst. However, under more typical catalytic conditions where the substrate to catalyst ratio is greater than unity, fewer than two electrons are consumed by each H_2O_2 molecule. These conditions are also those which would favor the participation of the hydroxyl radicals generated in reaction 4 in reactions other than reaction 5 such as the oxidation of the $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ anion. It therefore seems plausible to connect the decrease in the electrons consumed per H_2O_2 molecule with the appearance of the oxidized, Fe(IV) form of the heteropolyanion. The steady-state radiolysis of solutions containing both H_2O_2 and $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ (Figure 3) showed that the Fe(IV) form of the heterpolyanion was rapidly reduced by reaction with H_2O_2. This observation provides a possible explanation for the consumption of fewer than two electrons per H_2O_2 molecule during its electroreduction as catalyzed by $H_2OFe^{III}SiW_{11}O_{39}^{5-}$. One possible reaction sequence that accommodates this result is reactions 2–4 followed by

$$H_2OFe^{III}SiW_{11}O_{39}^{5-} + OH \rightarrow OFe^{IV}SiW_{11}O_{39}^{6-} + H_2O + H^+ \quad (6)$$

$$OFe^{IV}SiW_{11}O_{39}^{6-} + H_2O_2 + H^+ \rightarrow H_2OFe^{III}SiW_{11}O_{39}^{5-} + O_2H \quad (7)$$

$$O_2H \rightarrow 0.5O_2 \rightarrow 0.5H_2O_2 \quad (8)$$

The sum of reactions 2–4 plus 6–8 yields

$$1.5H_2O_2 + H^+ + e^- \rightarrow 0.5O_2 + 2H_2O \quad (9)$$

Only 0.67 electrons are consumed per molecule of H_2O_2 during the catalyzed electroreduction according to this reaction scheme, which is appropriate at pH values below 4 where the superoxide generated in reaction 7 is protonated.[10] The number of electrons consumed per molecule of H_2O_2 during an electrolysis will depend on the partitioning of the OH radicals generated in reaction 4 between reactions 5 and 6. Whenever reaction 5 is dominant, the catalyzed electrolysis results in the consumption of two electrons per H_2O_2 molecule just as is obtained if $Fe(OH_2)_6^{3+}$ is employed as the catalyst.[5] When reaction 5 proceeds in parallel with reaction 6 followed by reactions 7 and 8, fewer than two electrons per H_2O_2 molecule are consumed. Thus, the observed values of between 0.9 and 2 electrons consumed per molecule of H_2O_2 during its catalyzed electroreduction at the potential of the first reduction wave of the $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ catalyst can be accounted for on the basis of the partitioning of OH radicals between reactions 5 and 6. The simple, two-electron stoichiometry obtained when the electrolysis is carried out at more negative potentials, where the catalyst exhibits a two-electron reduction wave, is also understandable because the hydroxyl radicals are then generated in the presence of the Fe(II), not the Fe(III), form of the catalyst and their subsequent rapid reduction by the multiply reduced catalyst avoids the formation of the Fe(IV) complex and involves two electrons per H_2O_2 molecule.

Note that the sum of reactions 6 and 7 yields reaction 10. Thus, the same overall stoichiometry leading to the consumption of fewer than two electrons per H_2O_2 molecule would result if the hydroxyl radical produced in reaction 4 oxidized a H_2O_2 molecule instead of a Fe(III) center as in reaction 6. However, under these conditions, the rate of reaction 10 is apparently smaller than that of reaction 6. If this were not the case, the presence of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ could not have resulted in the observed decrease in the rate of electroreduction of H_2O_2 as catalyzed by $Fe(OH_2)_6^{2+}$ (Table II). These observations are consistent with the known rate constants for reaction 10, 4.5×10^7 M^{-1} s^{-1},[15] and the rate constant estimated for reaction 6 from the pulse-radiolysis experiments, 7×10^8 M^{-1} s^{-1}. Although the rate constant for reaction 5 was not measured, it seems likely to be comparable or somewhat larger than that for reaction 6 by comparison with the corresponding rate constants for the reactions of $Fe(OH_2)_6^{3+}$ and $Fe(OH_2)_6^{2+}$ with OH.[19] Thus, partitioning of the OH radicals generated in reaction 4 between reactions 5 and 6 provides a reasonable scheme to account for the experimental observations.

$$OH + H_2O_2 \rightarrow O_2H + H_2O \quad (10)$$

Electrocatalysts often achieve their activity through their ability to stabilize high-energy intermediates that are inevitably encountered in multiple-electron processes. In the present instance the high-energy species to be stabilized is the hydroxyl radical and the oxidized intermediate that we have depicted as $OFe^{IV}SiW_{11}O_{39}^{6-}$ could be regarded as a (deprotonated) hydroxyl radical stabilized by binding to an Fe(III) center. This viewpoint could be emphasized by replacing reactions 4 and 6 with the concerted, two-electron reaction 11. The consumption of fewer than two electrons per H_2O_2 molecule during catalyzed electroreductions of H_2O_2 would then be based on the partitioning of the $OFe^{IV}SiW_{11}O_{39}^{6-}$ complex between reaction 7 and reaction 12. As before, the stoichiometry would vary between 0.67 and 2.0 electrons per H_2O_2 molecule as the reaction sequence varied between reactions 2 + 3 + 11 + 7 and reactions 2 + 3 + 11 + 12, respectively.

$$H_2O_2Fe^{II}SiW_{11}O_{39}^{6-} \rightarrow OFe^{IV}SiW_{11}O_{39}^{6-} + H_2O \quad (11)$$

$$OFe^{IV}SiW_{11}O_{39}^{6-} + H_2OFe^{II}SiW_{11}O_{39}^{6-} + 2H^+ \rightarrow 2H_2OFe^{III}SiW_{11}O_{39}^{5-} \quad (12)$$

pH Dependence of H_2O_2 Disappearance during Steady-State Radiolysis. The concentration of H_2O_2 decreased much more rapidly at pH 5–7 than at pH 2 during steady-state radiolysis of N_2O-saturated solutions of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ (Figure 3). This difference seems likely to be associated with the difference in the reactivities of O_2^- and HO_2 (produced in reaction 7) toward $H_2OFe^{III}SiW_{11}O_{39}^{5-}$. The pulse radiolysis of oxygen-saturated formate solutions containing $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ at pH 7 showed that O_2^- readily reduces the Fe(III) center to Fe(II). This observation suggests that the following chain mechanism, resulting in the catalyzed disproportionation of H_2O_2, operates during the steady-state radiolysis of N_2O-saturated solutions of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ at pH ≥ 5 under conditions where the initial reaction is between OH and $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ to produce the Fe(IV) form of the heteropolyanion (reaction 6):

$$OFe^{IV}SiW_{11}O_{39}^{6-} + H_2O_2 \rightarrow H_2OFe^{III}SiW_{11}O_{39}^{5-} + O_2^- \quad (13)$$

$$H_2OFe^{III}SiW_{11}O_{39}^{5-} + O_2^- \rightarrow H_2OFe^{II}SiW_{11}O_{39}^{6-} + O_2 \quad (14)$$

These reactions are followed by reactions 3, 4, and 6, which regenerate the Fe(IV) form of the ion. The sum of reactions 13 and 14 plus 3, 4, and 6 is

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(19) *Natl. Stand. Ref. Data. Ser. (U.S. Natl. Bur. Stand.)* **1977**, *59*.

$$2H_2O_2 \rightarrow O_2 + 2H_2O \qquad (15)$$

Thus, this reaction sequence can account for the removal of H_2O_2 at a rate greater than that for the radiolytic generation of OH radicals at pH ≥5 (Figure 3). Reactions that would act to interrupt the chain are reactions 5, 8, and 12 as well as

$$2OH \rightarrow H_2O_2 \qquad (16)$$

$$O_2^- + OH \rightarrow O_2 + OH^- \qquad (17)$$

and[20]

$$O_2H + OH \rightarrow H_2O_3 \rightarrow O_2 + H_2O \qquad (18)$$

The rate constant for all of these chain-terminating reactions would be expected to be large. However, all of these reactions are second order in reactants that are present at very low concentrations so that the reaction rates would be relatively small compared with those of the chain-propagating reactions (reactions 3, 4, 6, 13, and 14), which all involve reactants ($H_2OFe^{III}SiW_{11}O_{39}^{5-}$ or H_2O_2) present at much higher concentrations. Thus, it seems plausible that the chain mechanism outlined above is responsible for the enhanced rate of H_2O_2 disappearance during steady-state radiolysis of mixtures of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ and H_2O_2 at pH 5–7.

Nature of the Complex Formed by One-Electron Oxidation of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$. In a recent study of the oxidation of $Fe^{III}(OH)_4^-$ by hydroxyl radicals, the product was formulated as a ferryl complex, $Fe^{IV}O(OH)_n$.[15] The differences in the spectra of $Fe^{IV}O(OH)_n$ and the oxidized species obtained during the pulse radiolysis of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ in the present study (Figure 2), specifically the shift toward the blue region of λ_{max}, may be a result of the much lower pH at which the spectrum in this report was obtained or of the differences in the coordination environment of the iron center in the two complexes. There is less uncertainty about the coordination environment of the iron center in the present case because the five oxo groups coordinated to the iron center that are also part of the polyoxometalate structure are inert toward substitution. A seven-coordinate Fe(IV) complex formed in an inner-sphere electron-transfer reaction to a coordinated OH radical cannot be ruled out, but a more likely reaction pathway would be hydrogen atom abstraction from the water molecule coordinated to the Fe(III) center by uncoordinated OH radicals. A mechanism involving simple outer-sphere electron transfer to OH is also possible but seems less likely because the rate of the reaction between $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ and OH decreases somewhat when the pH is increased from 4 to 7 (Table I). The formal potential of the Fe^{IV}/Fe^{III} couple almost certainly becomes less positive as the pH increases because of the difference in the degree of protonation at the iron center in the two oxidation states, so that the driving force for the reaction of the Fe(III) center with OH should increase with pH. That the rate decreases instead of increasing with pH could be regarded as evidence against simple outer-sphere electron transfer and, therefore, as mildly supportive of a hydrogen atom transfer mechanism.

The second-order constant governing the decomposition of the Fe(IV) intermediate began to exhibit a dependence on the concentration of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ at concentrations below ca. 0.1 mM (Table II). The overall kinetic behavior of the decomposition can be rationalized by reactions 19–21. Reaction 19 is an

$$H_2OFe^{III}SiW_{11}O_{39}^{5-} + OH \rightleftarrows HOFe^{IV}SiW_{11}O_{39}^{6-} + H_2O \qquad (19)$$

$$2HOFe^{IV}SiW_{11}O_{39}^{6-} + 2H_2O \rightarrow 2H_2OFe^{III}SiW_{11}O_{39}^{5-} + H_2O_2 \qquad (20)$$

$$HOFe^{IV}SiW_{11}O_{39}^{6-} + OH + H_2O \rightarrow H_2OFe^{III}SiW_{11}O_{39}^{5-} + H_2O_2 \qquad (21)$$

equilibrium that lies far to the right at concentrations of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ above ca. 0.1 mM so that the formation of the Fe(IV) complex is first order in the concentration of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$. The predominant pathway for the disappearance of the Fe(IV) complex is reaction 20, but at concentrations of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ small enough for reaction 19 to be incomplete, reaction 21 (and even reaction 16) could provide an additional pathway for the consumption of the Fe^{IV} complex, which would result in the observed increase in the apparent second-order rate constant for reaction 20.

Attempts to generate the Fe(IV) complex electrochemically were unsuccessful: No anodic processes were evident in scans to the most positive accessible potentials (1.5 V vs NHE) with solutions of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ at the highest pH values at which the complex was stable (pH <8). Upper and lower limits on the formal potential of the Fe^{IV}/Fe^{III} couple can be estimated on the basis of the observation that the Fe(III) complex is rapidly oxidized by OH and that the Fe^{IV} complex is reduced by H_2O_2. For half-reaction 22, these limits are $1.44 < E_f$ (vs NHE) < 2.65 (pH

$$OFe^{IV}SiW_{11}O_{39}^{6-} + 2H^+ + e^- = H_2OFe^{III}SiW_{11}O_{39}^{5-} \qquad (22)$$

0) or $0.61 < E_f < 1.82$ (pH 7). The failure to observe the anodic oxidation of $H_2OFe^{III}SiW_{11}O_{39}^{5-}$ could be the result of the inaccessibility of a significant portion of this potential range or of the kinetic sluggishness of the electrode process when proton transfer accompanies electron transfer or both.

One of the potentially most interesting aspects of the putative $OFe^{IV}SiW_{11}O_{39}^{6-}$ complex is its possible utility as a catalyst in oxidation reactions. The high rate constant for the reaction of the oxidized complex with itself (Table I) limits its utility as an oxidation catalyst. This high rate of decomposition of the Fe(IV) complex may be the reason that the Co- and Mn-substituted but not the Fe-substituted Keggin ion derivatives were reported to serve as efficient catalysts for the epoxidation of olefins by oxygen atom donors such as iodosylbenzene.[21] If the Fe(IV) complex examined in this study were generated by the reaction with iodosylbenzene, it would be likely to decompose more rapidly than it reacted with olefins. Heteropolytungstates substituted with other oxidizable transition metals are being investigated in continuing studies to determine if longer lived catalysts can be prepared and exploited.

Acknowledgment. The work at Caltech was supported by the National Science Foundation. J.E.T. was the grateful recipient of a graduate fellowship sponsored by BP America. The pulse-radiolysis studies were carried out at Bookhaven National Laboratory under Contract DEAC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

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